Pyroelectrocatalytic disinfection using the pyroelectric effect of low Curie temperature, lead-free ferroelectric ceramics

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I. Introduction

In recent years there has been an increasing interest in the use of pyroelectric materials for applications in electrochemical catalysis, as they have the potential to convert temperature fluctuations into electrical energy.

Broadly, this work explores using low Curie temperature (T_c), lead-free, ferroelectric ceramics for pyroelectric-electrochemical catalytic reactions, such as water splitting for hydrogen generation [1,2], decontamination of water [3,4,5] and disinfection of water [6,7].

The work detailed here investigates barium strontium titanate (BST) for the application of pyroelectrocatalytic water disinfection. BST has desirable pyroelectric properties for disinfection of water, with a high pyroelectric coefficient (p) and a low T_c of ≈35°C. BST also has the environmental and sustainability advantage of being a lead-free material comprising earth abundant elements. Additionally, (due to the low T_c of BST) the temperature fluctuations could be achieved using low grade waste heat or natural daily temperature fluctuations.

Previously published work has focused on the use of pyroelectric materials in nano-/micro- particle [6,7] or nanorod/nanofiber [4] forms. In this work, BST powders (1-2μm) and freeze cast porous structures were investigated. The BST powders were used initially for proof of concept for pyroelectrocatalytic disinfection of water. Subsequently, porous BST structures were used as a way of maintaining a high surface area but providing a potential solution to and minimising further contamination of the water with nano- and/or micro- particulates.

II. Methods/Results/Discussion

BST particles were synthesised and used to produce a variety of materials structures, including finely ground powders (1-2μm), porous structures and dense materials. Freeze casting was used to produce porous materials with aligned pore structures which are beneficial for providing high polarisation [8] and pore channels for high surface area contact with the water. The powders were analysed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The dense and porous structures were characterised using XRD, SEM, and electrical impedance spectroscopy (EIS) at a range of temperatures. Example SEM micrographs of the porous structures are shown in Figure 1. Measurements of polarisation–electric field (P-E) ferroelectric hysteresis loops and d_{33} after poling were undertaken to confirm the ferroelectric properties. The P-E ferroelectric hysteresis loops were measured at a range of temperatures and the remnant polarisation was used to calculate the pyroelectric coefficient of the dense and porous BST. P-E hysteresis loops for dense BST at a range of temperatures (0°C to 70°C) is shown in Figure 2.

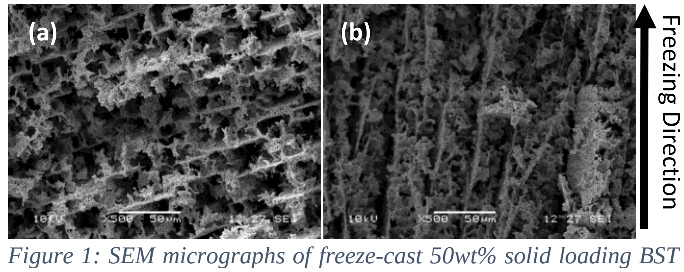

Figure 1: SEM micrographs of freeze-cast 50wt% solid loading BST ceramics. Pores are shown (a) perpendicular and (b) aligned parallel to the direction of freezing.

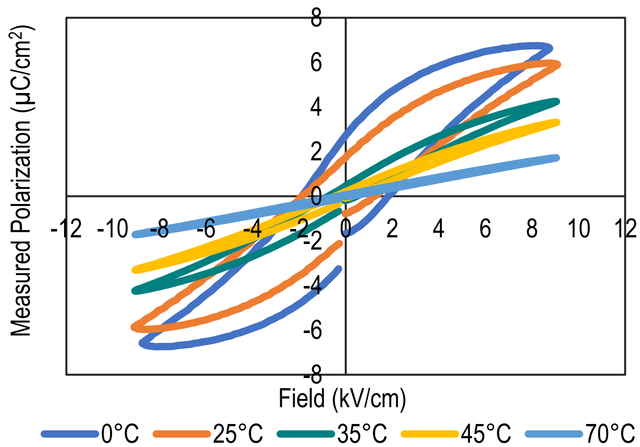

Figure 2: P-E hysteresis loops for BST dense pressed tablet at a range of temperatures from 0°C to 70°C.

In this work, the powders and porous pyroelectric materials are used as an ‘internal’ charge source, placed in direct contact with the solution containing bacteria [7] to examine the potential of using temperature fluctuations for disinfection of water. Preliminary experiments were carried out using Escherichia coli (E. coli) strains BW25113 and NCTC 10418 in the presence of BST powders. Vials containing the bacteria and particles, alongside control vials containing the bacteria only, were thermally cycled six times from 25°C-45°C.

Following the thermal cycling, aliquots were taken from the sample and control vials and diluted down to 10^{-8}. Three 10µl aliquots of each dilution were spotted onto agar plates and allowed to grow over night. The effectiveness of the pyroelectric BST powders for decontamination of the solutions was measured by counting and comparing the colony forming units (CFU) grown from the samples prior to and following the temperature cycling, as shown in Figure 3. The CFU/ml is calculated using the following equation:

$$CFU\ per\ ml\ = \frac{no.of\ colonies \times dilution\ factor}{amount\ of\ solution\ on\ plate\ (ml)} \quad (1)$$

Following these promising preliminary results, further experiments were carried out using the BST powders and porous structures. An orbital shaker was used to improve and maintain suspension of the particles in solution during the thermal cycling. The progression to the use of the sintered porous materials ensured that a high surface area was maintained while also improving the ease of removal and reuse of the BST material.

Further experiments were also carried out using less temperature sensitive strains of E. coli, such as NCTC 10418, as well as other bacteria types and indicators commonly found in contaminated water.

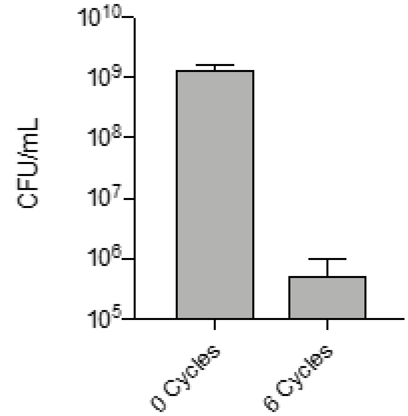

Figure 3: Viable cell counts of Escherichia coli (strain BW25113) in the presence of pyroelectric BST particles after 0 and 6 temperature cycles (25°C-45°C).

III. Conclusions

Physical and ferroelectric characterisation of the BST powders, novel porous structures and dense pressed pellets was successfully carried out.

The preliminary decontamination of water results were very promising, showing a significant 3-log reduction in viable bacterial cell counts (in CFU/ml). Within microbiology-based applications such as water decontamination and wound care a 3-log reduction is “gold standard”.

Further experiments were carried out with the pyroelectric BST powders and porous structures, using less temperature sensitive strains of E. coli as well as other bacteria and indicators commonly found in contaminated water.

Overall, BST powders and porous structures were successfully used in the pyroelectrocatalytic disinfection of cultured bacteria in solution. Further work will be carried out to optimise the materials and processes and future work will involve experiments using samples of waste and effluent water.

IV. References

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